

Synthesis, Structure, and Spectral Characterization of Cu(II) Complexes of Thiocarbohydrazide and Derivates

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Abstract

The synthesis and structure of thiocarbohydrazide and metal complexes of thiocarbohydrazone ligand are described. The ligand was obtained by condensation of N,N'-thiocarbohydrazide with salicylaldehyde. The Cu(II) complex have been synthesized by reacting $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and Ligand by molar ratio 2:1(M:L), while the Cu(II) complex of thiocarbohydrazide have been synthesized by reacting $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and TCH by molar ratio 1:2(M:L). These complexes are soluble only to a larger extent in DMF and DMSO. The bonding sites are the azomethine nitrogen atom, phenolic oxygen atom and thiol sulfur atom. The metal complexes exhibit square planar and octahedral structure. Characterization and structure elucidation of the synthesized compounds were achieved by spectral (IR, electronic, ^1H and ^{13}C NMR) as well as molar conductivities.

Keywords: Thiocarbohydrazide, Thiocarbohydrazone ligand, Cu(II) Complexes, ^1H and ^{13}C NMR.

1. Introduction

Thiocarbohydrazide (TCH) one of the simplest hydrazine derivatives of thiocarbonic acid, is an important chemical intermediate in organic synthesis and is used in the industrial production of insecticides, fungicides and various agricultural chemicals as well as in chemical laboratories as a chemical reagent [1,2]. Thiocarbohydrazide constitute an important class of N, S donor ligands possessing interesting chemical, biological and medicinal properties [3,4]. Thiocarbohydrazide derivatives have attracted much attention in recent years due to their applications in the synthesis of heterocyclic compounds [5,6] synthesis of 1,2,4-triazole [7-9], synthesis of transition metal complexes, [10] and in pharmacological studies [11]. Both hydrazine groups of thiocarbohydrazide are very reactive and predominantly form bis derivatives with aldehydes and ketones [12]. Hydrazone-based Schiff bases are versatile ligands capable of generating a variety of molecular architectures, coordination compounds, and polymerization catalysts [13]. Metal complexes of thiocarbohydrazones have attracted much attention due to their biological activity [14,15].

The aim of the present work is to study preparation of thiocarbohydrazide and the chelating behavior of TCH and the thiocarbohydrazone ligand towards transition metal copper(II). The structures of the ligand and metal complexes were characterized by FT-IR, ^1H and ^{13}C NMR and electronic spectra as well as conductivity measurements at room temperature.

2. Experimental:

2.1. Materials: copper(II) was used as chloride salt and was SCP, hydrazine hydrate, potassium hydroxide and salicylaldehyde were Sigma Aldrich, carbon disulfide was Riedel-deHaen, Organic solvents (ethanol, methanol, diethyl ether and dimethylformamide (DMF)) were Euro lab and were used without further purification.

2.2. Measurements: FT-IR spectra were recorded on a Jasco-Japan 410 spectrometer ($4000\text{--}400\text{ cm}^{-1}$) in KBr pellets. Electronic spectra were recorded at room temperature on a Hitachi UV/Vis spectrophotometer as DMF solutions. The ^1H and ^{13}C NMR spectra, as solutions in DMSO- d_6 , were recorded on a Bruker 400 MHz spectrometer at room temperature using TMS as an internal, Molar conductivities of 10^{-3} M solutions of the solid complexes in DMF were measured on the Corning conductivity meter NY 14831 model 441.

2.3. Synthesis of thiocarbohydrazide: A specified quantity (1.5 mol) of 50-60% aqueous hydrazine hydrate was placed in the flask. The temperature was lowered to 10°C and the stirring rate was controlled to 800 rpm, 30.15 ml of CS_2 (0.5 mol) were added dropwise over about one hour while maintaining the temperature below 15°C . After addition the reaction mixture continued to be agitated for 30 min at room temperature. The resultant mixture was refluxed at 70°C for 6 h. The reaction mixture was cooled to room temperature and the crystalline precipitate separated from liquid by filtration then Recrystallization by water, the TCH crystals were dried at 110°C . m.p $172\text{--}174^\circ\text{C}$.

2.4. Synthesis of thiocarbohydrazone ligand H_3L : A mixture of 2-hydroxy-1-benzaldehyde, (3.27 g, 19 mmol) and thiocarbohydrazide (1 g, 9.43 mmol) in absolute ethanol was refluxed for 3 h. where a yellow precipitate was formed on hot, then allowed to cool slowly and collected by filtration, washed with ethanol then diethyl

ether, air-dried and recrystallized from ethanol. The crystalline ligand was kept in a desiccators until used. The analytical and physical data for the H_3L ligand and its metal complexes are listed in Table (2,3).

2.5. Synthesis of Cu(II) complex of thiocarbohydrazide: To a hot methanolic solution (20 mL) of TCH (8 mmol, 0.85 gr) was added $CuCl_2 \cdot 2H_2O$ (4 mmol, 0.68 g) and the mixture was refluxed for 3 h till it became homogeneous. A few drops of triethylamine were then added to become $PH=8$ and cause precipitation and the refluxing was continued for additional 2 h. The solvent was removed by filtration, which afforded dark green precipitate. It was washed with methanol and dried in vacuum.

2.6. Synthesis of the $[Cu_2(SATCH)Cl_4]$: Potassium hydroxide, KOH (0.142 gr, 3.38 mmol) in the least amount of methanol (10 mL) was added gradually with constant stirring to the solution of the ligand, H_3L , (0.7 gr, 1.69 mmol) in ethanol (30 mL), in molar ratio 2:1(KOH: H_3L). Copper chloride Dihydrate, $CuCl_2 \cdot 2H_2O$ (0.457 g, 1.69 mmol) in ethanol (30 mL) was added gradually with constant stirring to the above mixture. The resulting mixture was refluxed for 3 h. A greenish black precipitate was formed, filtered off and washed several times with small amounts of methanol, ethanol then diethyl ether and finally air-dried. The yield was 0.8 g m.p. > 340°C.

3. Results and discussion

3.1. Characterization of the TCH:

The characteristic peaks at $1530-1488\text{ cm}^{-1}$ are assigned to coupled modes consisting principally of N-H wagging and C-N stretching vibrations. The C=S stretching vibration contributes to the two peaks $1184-756\text{ cm}^{-1}$. The H-N-H stretching vibration contributes to the two peaks $3273-3203\text{ cm}^{-1}$.

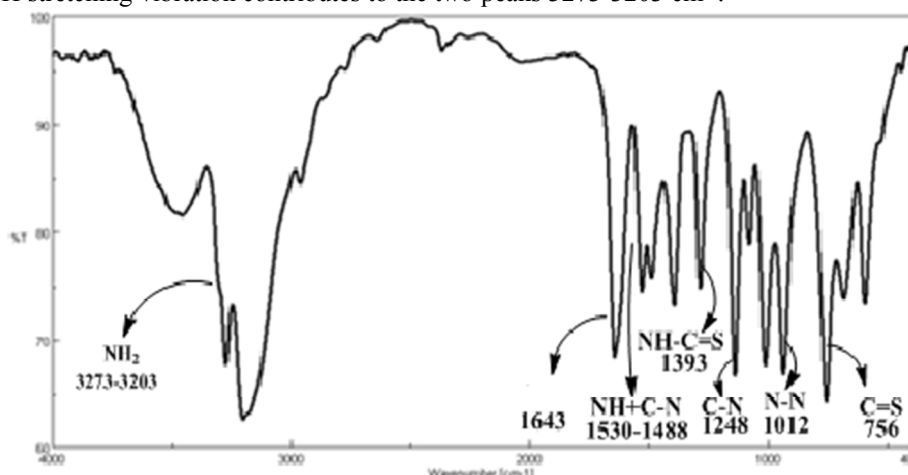


Figure.1. FT-IR spectral of TCH

The electronic spectrum of the TCH in DMF showed one band at 305 nm. This band may be assigned to $\pi \rightarrow \pi^*$ and $(n \rightarrow \pi^*)$ transitions of (C=S) groups. 1H and ^{13}C NMR spectral data (δ ppm) of the TCH relative to TMS (0 ppm) in DMSO- d_6 , The signal observed at 4.47 ppm may be due to H-N-H protons (4H). The signals observed at 8.68 ppm may be due to the NH protons (2H). This is supported by the ^{13}C NMR spectrum that showed one signal at 181.79 ppm that may be assigned to C=S.

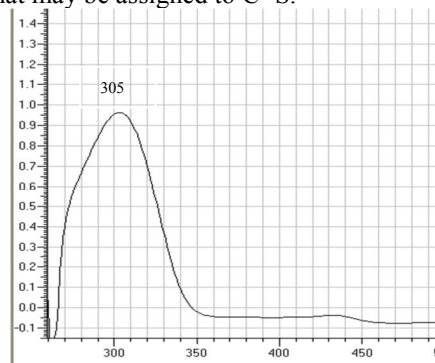


Figure.2. UV spectral of TCH

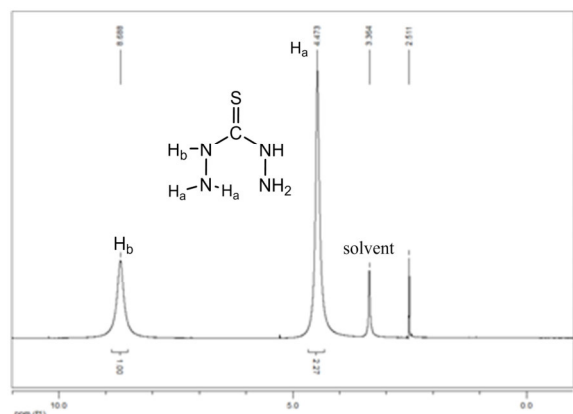


Figure.3. ^1H NMR of TCH

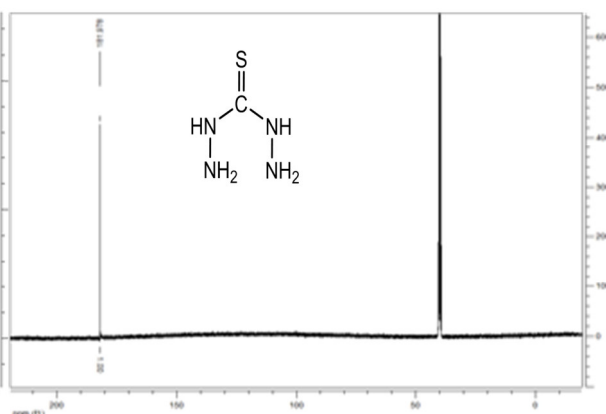


Figure.4. ^{13}C NMR of TCH

3.2. Characterization of the Thiocarbohydrazone (H_3L):

The structure of the ligand was elucidated by IR, electronic and ^1H and ^{13}C NMR spectra. The IR spectrum of the ligand showed bands at 3425, 3228, 1620 and 1284 cm^{-1} that may be assigned to $\nu(\text{OH})$, $\nu(\text{NH})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{O})$ phenolic, respectively. The appearance of the bands characteristic to $\nu(\text{C}=\text{S})$ in addition to the absence of an IR band around 2600 cm^{-1} due to $\nu(\text{SH})$ support the thione nature of the ligand in the solid state. The electronic spectrum of the ligand in DMF showed two bands at 345 and 400 nm. The first bands may be assigned to $\pi \rightarrow \pi^*$ transitions of the aromatic benzene ring and the $(\text{C}=\text{N})$ and $(\text{C}=\text{S})$ groups while the last band may be assigned to transitions of $(n \rightarrow \pi^*)$ to the $(\text{C}=\text{N})$ and $(\text{C}=\text{S})$ groups. ^1H and ^{13}C NMR spectral data (δppm) of the ligand relative to TMS (0 ppm) in $\text{DMSO}-d_6$, lend further support of the suggested structure of the ligand. The signals observed at 9.86 ppm may be due to the phenolic OH protons. The signals observed at 9.74 ppm may be due to the NH protons. Also, signals observed at 8.32 ppm may be due to protons of the $\text{HC}=\text{N}$ groups. The aromatic protons showed signals in the range 6.8–7.99 ppm. This is supported by the ^{13}C -NMR spectrum that showed signals at 176, 156 and 139.88 ppm that may be assigned to $\text{C}=\text{S}$, $\text{C}=\text{O}$ and $\text{C}=\text{N}$ groups, respectively.

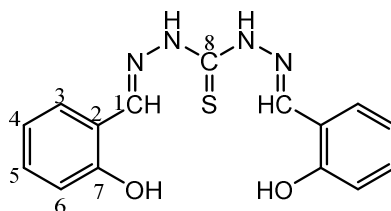


Figure.5. structure of H_3L

Table 1. ^{13}C NMR spectral data (ppm) for H_3L ligand ($\text{DMSO}-d_6$):

Group	1	2	3	4	5	6	7	8
Chemical shift	139.88 ppm	120.72 ppm	127.618 ppm	116.39 ppm	119.68 ppm	131.208 ppm	156.75 ppm	176.67 ppm

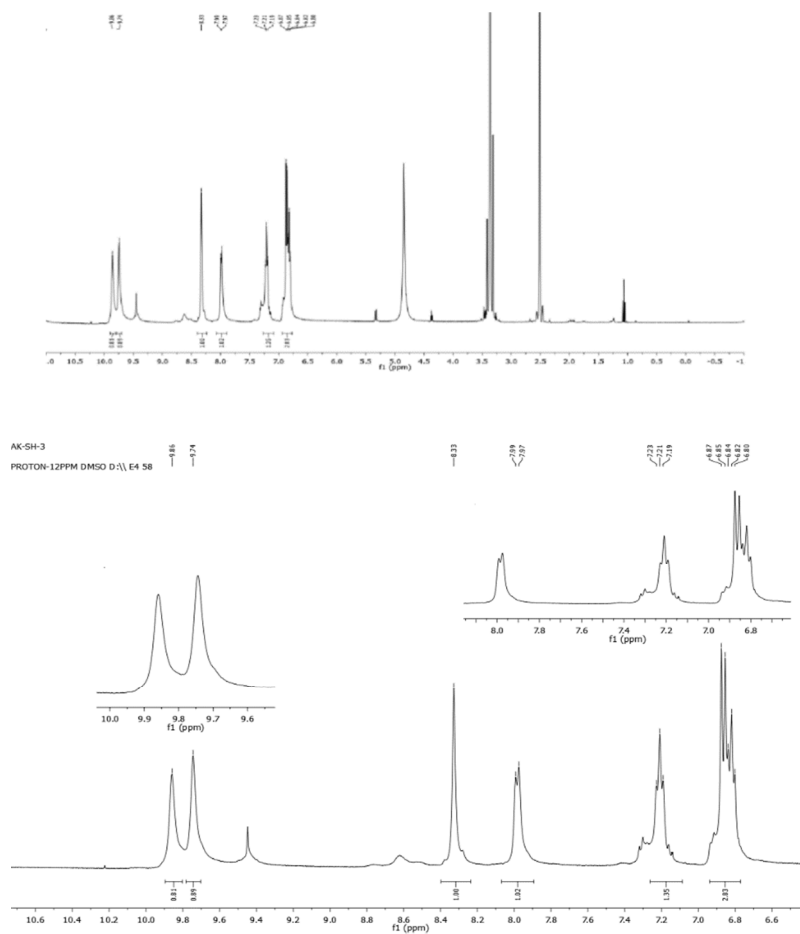


Figure.6. ^1H NMR of H_3L

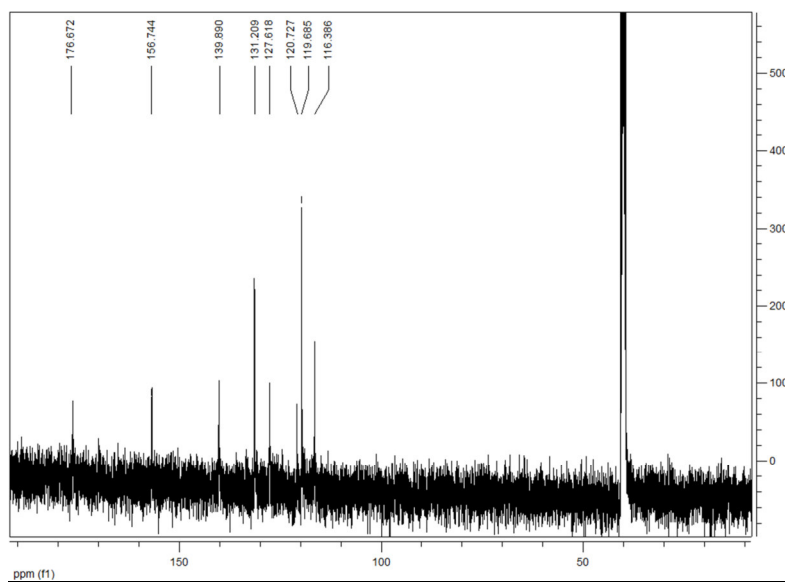


Figure.7. ^{13}C NMR of H_3L

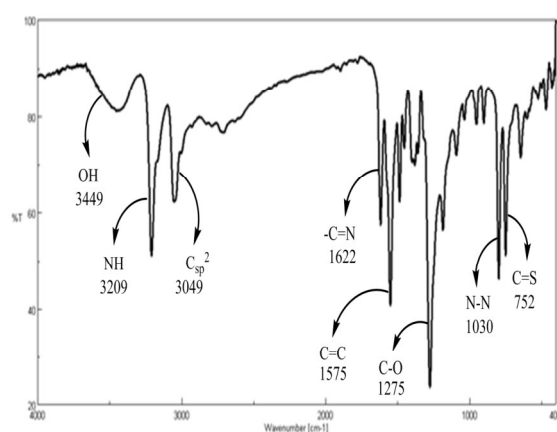


Figure.8.IR spectral of H₃L

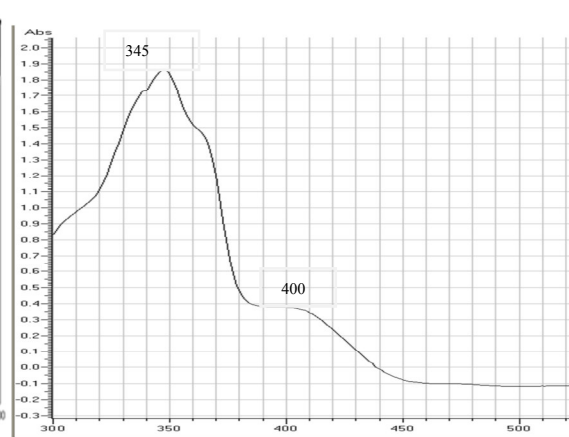


Figure.9.UV spectral of H₃L

3.2. Characterization of complexes:

3.2. 1.Characterization of copper complex with Thiocarbohydrazide[Cu(tch)₂]:

- IR spectra:

The IR spectral data of the complexes are listed in Table 2. Comparison of the IR spectra of the metal complex with that of the TCH revealed that complex showed bands in the range 3273–3203 cm⁻¹ which can be assigned to $\nu(\text{NH}_2)$ of the amine group of the TCH was shifted to lower frequencies (3254–3163). Although there are five donor sites, the TCH acts as a tridentate ligand. On moving from free TCH to [Cu(tch)₂] the $\nu(\text{N-H})$ is blue shifted (Table 2). The $\nu(\text{C=S})$ of TCH was shifted to high frequencies (770 cm⁻¹). A new band at 1620 cm⁻¹ assigned to (C=N). We have observed a strong band at 1505 cm⁻¹ that is intermediate between $\nu(\text{C-N})$ and $\nu(\text{C=N})$ indicating

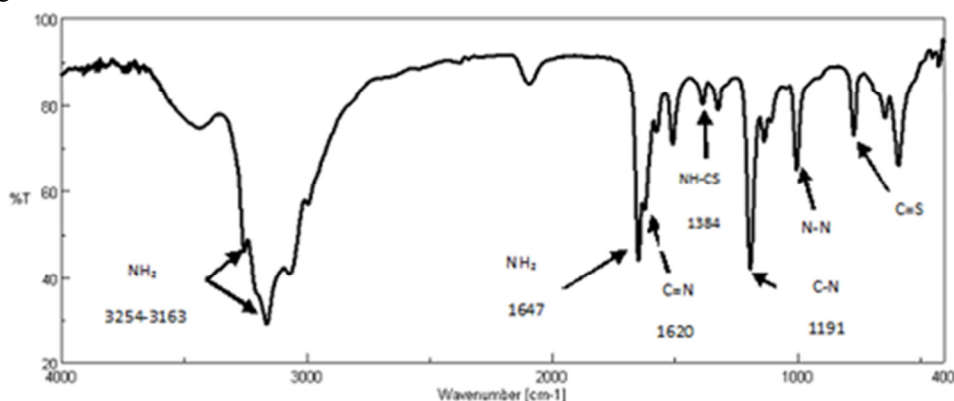


Figure.10.IR spectral of [Cu(tch)₂]

- Electronic spectral data and Conductivity measurements :

The electronic spectra of the [Cu(tch)₂] in DMF has one band at (430)nm. These band may be assigned to the transitions d-d. The molar conductance values of the complex in DMF (10⁻³ M solutions) were measured at room temperature and the results are listed in Table 3. The values show that the complex has non-electrolytic nature. this data refers that this complex has octahedral geometry.

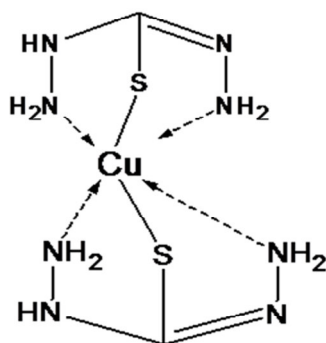


Fig.9.Suggested structure of $\text{Cu}(\text{tch})_2$

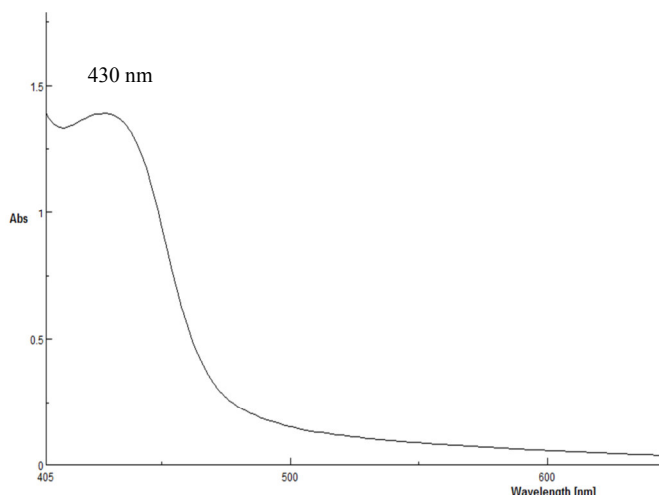


Fig.10.UV Spectral of $[\text{Cu}(\text{tch})_2]$

3.2.2. Characterization of copper complex with SATCH $[\text{Cu}_2(\text{SATCH})\text{Cl}_4]$:

FT- IR spectra:

The IR spectral data of the complexes are listed in Table 2. Comparison of the IR spectra of the metal complex with that of the free ligand revealed that the band at 3449 cm^{-1} assigned to $\nu(\text{OH})$ in the free ligand was shifted to lower frequencies (3435 cm^{-1}) in the complex,. Also, the band at 1622 cm^{-1} assigned to $\nu(\text{C}=\text{N})$ in the free ligand was shifted to lower frequencies (1603) in the complex, indicating the participation of the azomethine nitrogen in chelation .The $\nu(\text{C}-\text{O})$ phenolic of the free ligand at 1275 cm^{-1} was shifted to lower frequencies (1248 cm^{-1}) in the complex , suggesting the participation of the phenolic $-\text{OH}$ group in chelation .The bands assigned to $\nu(\text{C}=\text{S})$ in the free ligand remained unchanged or shifted to higher frequencies in the complex, indicating the nonparticipation of the $(\text{C}=\text{S})$ group in chelation.

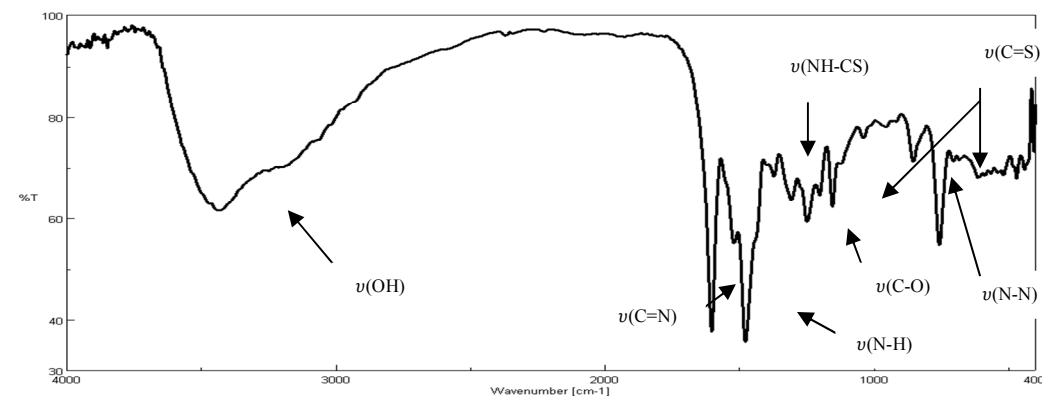


Figure.10.IR spectral of $[\text{Cu}_2(\text{SATCH})\text{Cl}_4]$

- Electronic spectral data and Conductivity measurements:

The data of the electronic spectra of the ligand and its complexes are given in Table 4. The spectrum of thiocarbohydrazone (H_3L) presented two bands in the UV interval at 348 nm assigned to $(\pi \rightarrow \pi^*)$, 400 nm assigned to $(n \rightarrow \pi^*)$ transitions respectively.

The electronic spectra of the $[\text{Cu}_2(\text{SATCH})\text{Cl}_4]$ in DMF has two bands at (338 nm) . These bands may be assigned to the transitions $(\pi \rightarrow \pi^*)$, 410 nm assigned to the transitions $(n \rightarrow \pi^*)$ and that have high intensity Comparison of the electronic spectra of the ligand ,that refer to $\text{L} \rightarrow \text{M}$.The values of Conductivity measurements show that the complex has non-electrolytic nature.

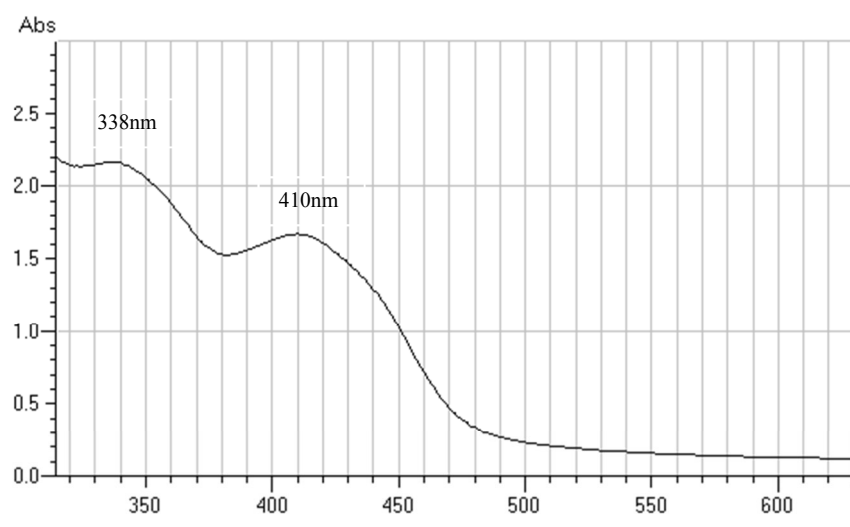
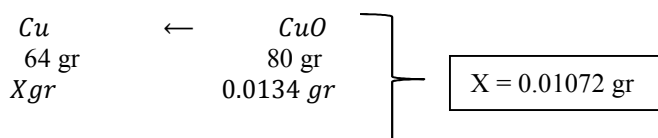


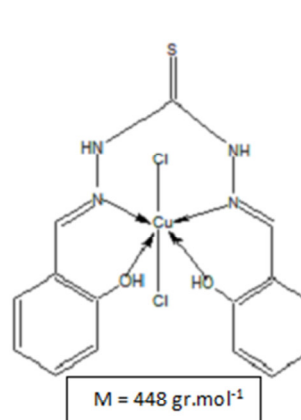
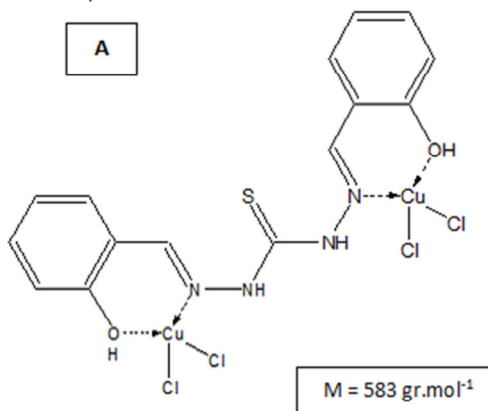
Fig.10.UV Spectral of $[Cu_2(SATCH)Cl_2]$

- Determination molar ratio of (M: L) by furnace :

Analyse of metal ions followed dissolution of the solid complex (0.0513 gr) in hot concentrated nitric acid, HNO_3 , then these sample were sintered at $900^\circ C$ for 1 h in a furnace (Carbolite Furnace, CWF 1200) and then cooled at room temperature in desiccators, after that we notice that the formed compound is CuO (Black color) (0.0134 gr).



So the complex contain (0.01072 gr) of copper metal , we suggest two structure of this complex and account the amount of copper in each of them and compare it with The practical value to determine the correct structure.



Compound A : molecular weight 592 gr contain 128 gr of copper metal Weight of disjointed sample 0.0513 gr contain y gr of copper metal	}	$Y = 0.01126 \text{ gr}$
Compound B: molecular weight 448 gr contain 64 gr of copper metal Weight of disjointed sample 0.0513 gr contain Z gr of copper metal	}	$Z = 0.0073 \text{ gr}$

When we compare between X,Y,Z, we notice that $X \cong Y$, So the complex has a dinuclear structure [A]

$$yeild = \frac{x}{y} = \frac{0.01072}{0.01126} = 95.2\%$$

Tabel-2- Characteristic infrared absorption frequencies (cm^{-1}) of the ligand and complexes.

complexes	$\nu(\text{NH}_2)_{\text{st}}$	$\nu(\text{NH}_2)_{\text{w}}$	$\nu(\text{N}-\text{H})_{\text{st}}$	$\nu(\text{C}=\text{N})$	$\nu(\text{NH}-\text{CS})$	$\nu(\text{C}=\text{S})$	$\nu(\text{C}_{\text{sp}^2}-\text{H})$	$\nu(\text{C}-\text{O})$	$\nu(\text{OH})$	$\nu(\text{M}-\text{N})$
TCH	3273-3203	1643	3180	-	1393	756 1184	-	-	-	-
$\text{Cu}(\text{TCH})_2$	3254-3163	1647	3069	1620	1384	770 1191	-	-	-	423
SATCH	-	-	3209	1622	1375	2	3049	1275	3449	--
$[\text{Cu}_2(\text{SATCH})\text{Cl}_2]$	-	-	3189	1603	1372	756 1155	3030	1248	3435	469

Table -3- Molecular weight and melting point of the ligand and complexes

Compounds	Mol.Weight	Colour	Yield	M.P.($^{\circ}\text{C}$)
Thiocarbohydrazide	106	White needles	70%	172-174
$[\text{Cu}(\text{tch})_2]$	275.4	Greenish black	45%	< 350
SATCH	314	yellow	75%	192-195
$[\text{Cu}_2(\text{SATCH})\text{Cl}_4]$	592	Dark green	35%	< 350

Table 4. Electronic spectral data , molar conductance and geometries of ligand and complexes

compounds	Electronic spectra (nm)	Assignment	geometry	Conductance ^a $\mu\text{S}/\text{cm}$
Thiocarbohydrazide	305	$n \rightarrow \pi^*$	-	-
$[\text{Cu}(\text{tch})_2]$	430	d-d	octahedral	20
SATCH	345 400	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-
$[\text{Cu}_2(\text{SATCH})\text{Cl}_4]$	338 410	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Square planner	30

a: Solutions in DMF (10^{-3} M) , at room temperature 25 $^{\circ}\text{C}$

Conclusions

In this research the preparation, isolation, and characterization of a new five-dentate Schiff basederived from thiocarbohydrazide and its complexes with Cu(II) have been carried out. It have beenproposed that the Schiff base ligand coordinates through the nitrogen of the azomethine group and the phenolic oxygen atom, while TCH coordinate through the amine group and sulfur atom forming a stable chelate complexes.

In the light of the above discussion, square planner geometry have been proposed for Cu(II) complexewith SATCH in molar ratio (1:2) (L:M), Whereas Cu(II) formed octahedral with TCH in (1:2) molar ratio(M:L) .

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